Eid AlSbou

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Outline

• Introduction
• Ambient MS
• DESI
• DART
• (DESI & DART)MS advantages
Mass Spectrometry

Ion Source → Mass Analyzer → Detector

Vacuum System → Sample → Date Analysis

Traditional Ionization Methods

- Gas-Phase Ionization
  - Electron Ionization (EI)
  - Chemical Ionization (CI)
- Particle Bombardment
  - Fast Atom Bombardment (FAB)
  - Secondary Ion Mass Spectrometry (SIMS)
- Atmospheric Pressure Ionization
  - Electrospray Ionization (ESI)
  - Atmospheric Pressure Chemical Ionization (APCI)
- Laser Desorption
  - Matrix-Assisted Laser Desorption Ionization (MALDI)
**Traditional Ionization Methods**

- The primary disadvantage to most traditional ionization methods are:
  1. The ions are formed in a vacuum environment
  2. The ions production requires a solvent (ESI), Matrix (MALDI)...
  3. Not applicable for in-situ analysis

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**Ambient Ionization**

- **Graham Cook** creates the term “Ambient Ionization Methods” in 2004 to describe developing techniques to analyze samples in their native state.
DESI

- Reported in 2004 by Graham Cook

Principle of operation

- DESI is a combination of electrospray (ESI) and desorption (DI) ionization methods.

$$(ES + D) \times I = DESI$$
DESI Mechanism

• In DESI there are two ionization mechanisms,
  – Ion/surface scattering
  – Charge droplets/surface

(cont.)

– Ion/surface scattering “low molecular weight molecules”
  • (diazao dye, steroids, caffeine, nitroaromatics, .. etc.)

\[
\begin{align*}
X^+_{(aq)} + A_{(s)} &\rightarrow X_{(aq)} + A^+_{(s)} \\
X^+_{(g)} + A_{(s)} &\rightarrow X_{(g)} + A^+_{(s)} \\
X^+_{(g)} + A_{(g)} &\rightarrow X_{(g)} + A^+_{(g)}
\end{align*}
\]
(cont.)

Charge droplets/surface “high molecular weight molecules” (proteins, peptides, oligosaccharide, .. etc.)

How?: The charged droplet hits the sample, spreads over a diameter greater than its original diameter, dissolves the analyte (e.g. protein) and rebounces. The droplets undergo declustering during travel to the MS inlet.

Electrospray like spectra; multiply charged ions

DESI applications

• Using DESI for a wide range of molecules from different surfaces:
  – Imaging
  – explosive agents
  – chemical warfare agents
  – amino acids
  – peptides
  – proteins
  – drug molecules
Prostate cancer indicating by DESI-imaging

imaging of prostate tissue showing areas of cancer and normal tissue in a sample ion image of m/z 465.4, cholesterol sulfate

DESI for Forensic

Forensic applications of DESI technique provides a valuable methods in analysis of toxic industrial compounds, chemical warfare agents, illicit drugs, explosive, inks, fingerprints and skin.
Direct analysis in real time (DART) was initially developed in 2003 and reported in 2005 – Very similar to DESI (gas solvent instead of liquid)

DART source
DART Ionization

Penning ionization
Sample ionized directly by energy transfer from metastables (M*)

Proton transfer (positive ions)
1. He⁺ ionizes atmospheric water
   \[ \text{He}^+(g) + \text{H}_2\text{O}(g) \rightarrow \text{He}(g) + (\text{H}_2\text{O})_{n-1}^+ \text{H}^+(g) + \text{OH}^- (g) \]
2. Ionized water clusters transfer proton to sample
   \[ [(\text{H}_2\text{O})_{n-1}^+ + \text{H}]^+ + M \rightarrow [\text{M}+\text{H}]^+ + n\text{H}_2\text{O} \]

Electron capture (negative ions)
1. Penning electrons rapidly lose their energies
   \[ e^-_{\text{fast}} + \text{gas} \rightarrow e^-_{\text{slow}} \]
2. Oxygen captures electrons
   \[ e^-_{\text{slow}} + \text{O}_2 \rightarrow \text{O}_2^- \]
1. \( \text{O}_2^- \) ionizes sample

DART-Mass spectra

- DART produces relatively simple mass spectra characterized by
- \( \text{M}^+ \); and/or \([\text{M}+\text{H}]^+ \) in **positive-ion** mode, and
- \( \text{M}^- \). or \([\text{M}-\text{H}]^- \) in **negative-ion** mode.
DART applications

- DART has same applications of DESI technique:
  - Forensics
  - Pharmaceutics
  - Food chemistry
  - Biological samples
  - Chemical analysis

DART for Pharmaceutical

TLC chromatogram of the extract of Evodiae fructus

DART-MS spectra of rutaecarpine and evodiamine.

rutacarpine

evodiamine

http://www.ecplaza.net/tradeleads/seller/3633462/evodiamine_98_99_hplc.html#none
DART for Biological

Fatty acid methyl ester (FAME) ions from Bacterial whole cells were generated by DART. Positive ion mass spectrum of (a) *E. coli* (Gram negative) and (b) *S. pyogenes* (Gram positive) acquired by direct DART-TOF MS analysis after in-situ thermal hydrolysis/methylation of the bacterial fatty acids to generate the corresponding FAMES, (1-18; FAMES).

DART for Chemical analysis

Mass spectra obtained with DART for cholesterol. The mass spectrum for cholesterol was performed by DART-TOF MS.
(DESI & DART)MS advantages

1. minimal sample preparation;
2. sample maintenance under ambient conditions outside the vacuum system;
3. Rapid
4. Sensitive
5. high-throughput analysis;
6. the ability for in-situ detection.
7. gentle ionization methods
8. used for both organic and biological compounds, polar and non-polar molecules.

References